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PATENT ABSTRACTS OF JAPAN

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(54) PROTON CONDUCTIVE THIN FILM ELECTROLYTE

(57)Abstract:

PURPOSE: To improve the ion conductivity of a thin film electrolyte.

CONSTITUTION: A proton conductive solid electrolyte [$\text{H}_3\text{PO}_4(\text{WO}_3)_{12}/29\text{H}_2\text{O}$, $\text{ZrO}(\text{H}_2\text{SO}_4)_{2/7}\text{H}_2\text{O}$, $\text{H}_3\text{OUO}_2\text{PO}_4/3\text{H}_2\text{O}$, etc.] is contained in or held by a high polymer fine porous film (normally, a carrier of alumina or the like is used,) and a proton conductive electrolytic solution is filled in the voids and is fixed. Ion conductivity level of no less than 10^{-3}S/cm is thus achieved.

LEGAL STATUS

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CLAIMS

[Claim(s)]

[Claim 1] The proton conductivity thin film electrolyte which is a solid thin film electrolyte substantially, and is characterized by making the solid electrolyte of proton conductivity which was filled up with the electrolytic solution of proton conductivity and was fixed during hole of a macromolecule fine porosity layer hold on a macromolecule fine porosity layer.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] this invention relates to a proton conductivity thin film electrolyte. When it states in detail, a proton conductive solid electrolyte is supported on a macromolecule fine porosity layer, and the application to electrolytes, such as an ordinary temperature type fuel cell and a water electrolysis, is expected about the thin film electrolyte which comes to sink in in an electrolytic solution during the hole further.

[0002]

[Description of the Prior Art] As a solid-state polyelectrolyte layer, there is an ion conductivity material represented by the complex of the ion exchange membrane and the polyethylene oxide (PEO is called below) which are represented by the layer (tradename NafionR) of a perfluoro carbon system with a sulfonic group, and an alkali-metal salt, it inquires widely, and the part is put in practical use. Since these layers are solid-states, they do not have a liquid leak, and it is easy to process them, and they have the advantage of being compact. It excels in a thermal property, since that ion exchange membrane, such as a perfluoro sulfonic acid and a perfluoro carboxylic acid, is chemical and the compact cell united with the positive electrode or the negative electrode can be constituted, it is used for a brine electrolysis, and the application to a fuel cell, a water electrolysis, etc. is also considered further. As for the complex of PEO and alkali-metal salts (LiCF₃SO₃, LiClO₄, LiAS F₆, etc.), the application to the big rechargeable battery and big primary cell of power density or an energy density, an electrochromic element, or a sensor is expected.

[0003]

[Problem(s) to be Solved by the Invention] By the system using a solid-state polyelectrolyte layer, there is a problem fall for the ohmic loss according [electrical energy luminous efficacy] to membranous electric resistance. Although the solid-state polyelectrolyte layer using an ion conductor like the complex of PEO and an alkali-metal salt has the advantage that it is a solid-state, as compared with aqueous-solution systems, such as a diffusion, alkali, and a salt, in ordinary temperature, a specific conductivity is low 2-3 figures, and intended use is limited from a constraint of a membranous ohmic loss. For example, the effective resistance of an electrolyte layer [as / whose specific conductivities in ordinary temperature are 10-6S and cm⁻¹ in a 50-micrometer thickness] is set to 5000ohmcm⁻¹. Although thin film-ization is one solution in order to lower electric resistance, there is mainly a limitation from a constraint of a dynamic intensity.

[0004] such a situation -- taking an example -- this invention persons -- the hole of a solid-state macromolecule porous material thin film -- although it examines solving the above-mentioned trouble by filling up with and fixing an electrolytic solution in inside, and constituting an electrolyte thin film and a success is stored, in order to aim at utilization of an electrolyte thin film, and an applied expansion, to raise ion conductivity more is desired (Refer to JP,1-158051,A and JP,2-291607,A)

[0005]

[Means for Solving the Problem] this invention offers the proton conductivity thin film electrolyte which is a solid thin film electrolyte substantially, and is characterized by making the solid electrolyte of proton conductivity which was filled up with the electrolytic solution of proton conductivity and was fixed during hole of a macromolecule fine porosity layer contain or hold on a macromolecule fine porosity layer, in order to attain the above-mentioned technical problem.

[0006] Although high ionic conductivity is obtained since an electrolytic solution is used in spite of being able to deal with substantially the electrolyte thin film which these people are indicating

previously like the above as a solid-state, ten to 3 S/about cm is still limit. On the other hand, $\text{H}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, $\text{ZrO}_2 \cdot (\text{H}_2\text{SO}_4)_2$ and $7\text{H}_2\text{O}$, $\text{H}_3\text{UO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$, etc. are known as a proton system ion-conductive-ceramics electrolyte, and the ion conductivity exceeding ten to 3 S/cm is also reported by these. However, these do not remain as they are and cannot necessarily be used as a fuel cell etc. as an electrolyte.

[0007] however, this invention — **** of the above — the usable electrolyte thin film of high ionic conductivity was able to be obtained to the fuel cell etc. by holding on a macromolecule fine porosity layer, and being filled up with the electrolyte of proton conductivity and fixing during hole, the proton system ion conductive electrolyte which has a high ion conductive ceramics. It was also enabled to obtain the high ionic conductivity which exceeds 10^{-3}S/cm as a solid-state substantially in the thin film electrolyte which can be dealt with by this.

[0008] For 0.1 microns – 50 microns and the rate of a hole, as a macromolecule fine porosity layer, 40 – 90% and breaking strength are [a thickness] 2 200kg/cm. That whose diameter of a mean breakthrough is 0.001 microns – 0.7 microns is used preferably above. A suitable thickness is 0.1–50 micrometers. Although influenced also by the layer material or the manufacture technique, generally, by less than 0.1 micrometers, it becomes disadvantageous in respect of a practical strength, or handling and workability, and if 50 micrometers is exceeded, effective resistance will become large.

[0009] The suitable rate of a hole is 40 – 90%. At 40% or less, there are too few amounts of a proton conductivity electrolytic solution, and sufficient ion conductivity is hard to be obtained. On the other hand, if 90% is exceeded, it will become difficult to obtain a practical thin film intensity. Breaking strength is 2 200kg/cm. The above is suitable. Breaking strength makes more difficult than this the parvus, sinking [film production and sinking in of the electrolytic solution] in, or manipulation processing that can be set as a product erector.

[0010] 0.001 micrometers – 0.7 micrometers are suitable for the diameter of a mean breakthrough. It becomes difficult for the parvus and an ion conductive ceramics to become small, and it to fix and carry out transudation prevention of the electrolytic solution, if the diameter of a mean breakthrough is too large on the other hand. As a material of a macromolecule fine porosity layer, polyethylene, polypropylene, a polycarbonate, a polyimide, polyester, tetrafluoro polyethylene, etc. can be used. Although a polyolefine, a polytetrafluoroethylene, and a polyvinylidene fluoride can be used from the field of chemical and an electrochemical stability as a material of a thin film, it is not limited to these. It especially faces using a polyolefine and weight average molecular weight is 5×10^5 . The above polyolefine is suitable.

[0011] As a proton conductivity solid electrolyte supported to a thin film, $\text{H}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, $\text{ZrO}_2 \cdot (\text{H}_2\text{SO}_4)_2$ and $7\text{H}_2\text{O}$, $\text{H}_3\text{UO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$, etc. can be used. Moreover, it is not limited to these. for example, about $\text{H}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, and $\text{ZrO}_2 \cdot (\text{H}_2\text{SO}_4)_2$ and $7\text{H}_2\text{O}$. There is a report of K.Mohapatra, G.D.Boyd, F.G.Storz, S.Wagner and F.Wudl, J.Electrochem.Soc.126 (1979) 805, etc. Ion ***** of 0.1 [S/cm] is reported by the room temperature. About $\text{H}_3\text{UO}_2\text{PO}_4$ and $3\text{H}_2\text{O}$, it is A.T.Howe, S.M.Sheffield, P.E.Childs and M.G.Shilton, and Thin Solid Films 67 (1980) 365. There is an example of a research and there is a report with the ionic conductivity of 5×10^{-3} [S/cm] at a room temperature.

[0012] Although also making a thin film support directly is considered, generally, minerals support is made to support a proton conductivity solid electrolyte, and it holds this to a thin film. What is known as catalyst supports, such as an alumina and a silica, as support can be used. Generally as particle size of support, an about 100–800nm ultrafine particle is good. The above-mentioned thin film is made to specifically fix first the alumina of an ultrafine particle (particle-size:10–80nm), or the support of a silica. As the fixed technique, temperature is raised and pressed, after sprinkling an ultrafine particle uniformly to ** thin film and removing excessive grain by the blower etc. Although temperature differs by the quality of the material and thickness of a thin film, generally about **15 degrees C near a glass transition temperature is desirable.

[0013] ** Infiltrate the precursor of ultrafine particle support, such as a silica and an alumina, into a thin film, and form a silica, an alumina, etc. by the reaction. What is necessary is just to have exposed so that it may be held at a thin film, and it may be under hole in short and an electrolytic solution can be contacted although **** can be carried out. As for the amount of a proton conductivity solid electrolyte, it is desirable to make [many / as possible] it. Proton conductivity electrolytes are the bearers with main ionic conductivity, and it is for raising ionic conductivity by making [many] the amount.

[0014] Fill up the hole of a thin film, and as an electrolytic solution, although the thing others of an indication can be directly used for the aforementioned part ** which these people have already indicated. For example, a benzonitrile, benzyl cyanide, a 1-phenyl-1-cyclopropane carbonitrile, DL-2 phenyl butyronitrile, 4-phenyl butyronitrile, 2, and 2-diphenyl propionitrile. Although the solution of the electrolyte which comes to add a proton donor to alkali-metal salts, such as at least one sort and lithium perchlorate of a polyethylene-glycol wood ether and a polypropylene-glycol wood ether, and a sodium perchlorate, and this is usable, it is not limited to this.

[0015] Although an electrolytic solution is proton conductivity in itself, it is during hole of the thin film holding a high proton conductivity solid electrolyte, and has the effect which lowers the interface impedance between high proton conductivity solid electrolytes, and the operation which gives gas-seal nature. The internal organization of the thin film electrolyte of this invention is typically shown in drawing 1. The support particle 2 is filled up with and held between the macromolecule network structures 1 of a fine porosity thin film, and the proton conductivity solid electrolyte is supported by the front face of this support particle 2. And the electrolytic solution 3 of proton conductivity is filled with the clearance where it remains under hole, and it is placed between the interface of a proton conductivity solid electrolyte.

[0016]

[Example]

After sprinkling the alumina ultrafine particle of 500nm of mean particle diameters on the 25 micron thick polyethylene fine porosity layer (41% of the rates of a hole, 0.25 micrometers of the diameters of a mean breakthrough, and breaking strength 250kg/cm²) which carried out the example 1 biaxial stretching, and was obtained, it pressurized with the hotpress at 120 degrees C for 60 minutes. Then, since the aqueous solution of 5%-H₃ PO₄12.29(WO₃) H₂ O was infiltrated, it was made to dry at 100 degrees C.

[0017] The solution which mixed the phosphoric-acid aqueous solution and the polyethylene-glycol wood ether by 1:8:1 85% to 2-phenyl butyronitrile was sunk into the obtained support thin film as an electrolytic solution. Consequently, the thin film support electrolyte with which ionic conductivity exceeded ten to 3 S/cm by 3x10 to 3 S/cm was obtained (45 micrometers of thickness).

[0018] In the thin film electrolyte produced without sinking in of an alumina ultrafine particle and H₃ PO₄12.29(WO₃) H₂ O like the above, ionic conductivity was 4.5x10 to 4 S/cm.

[0019] They are after inspersion and pressurization and the molybdophosphoric acid H₃ about a silica particle (diameter of 5.5 micrometer) to a polyethylene fine porosity layer like example 2 example 1. Propylene carbonate infiltrated the solution with which [PMo₁₂O₄₀] and nH₂ O consist 40wt%, and a phosphoric acid consists of 10wt% 50%, and produced the electrolyte thin film.

[0020] The ionic conductivity of this electrolyte thin film was 1.01x10 to 3 S/cm. It was the same as that of the above because of the comparison, and when the thin film electrolyte which does not sink in a silica particle and a molybdophosphoric acid was produced, ionic conductivity was 2.47x10 to 4 S/cm.

[0021]

[Effect of the Invention] The proton conductive thin film electrolyte of this invention can improve ionic conductivity in a solid thin film electrolyte on the real target which fixed the electrolytic solution during hole.

[Translation done.]

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Field

[Field of the Invention] this invention relates to a proton conductivity thin film electrolyte. When it states in detail, a proton conductive solid electrolyte is supported on a macromolecule fine porosity layer, and the application to electrolytes, such as an ordinary temperature type fuel cell and a water electrolysis, is expected about the thin film electrolyte which comes to sink in in an electrolytic solution during the hole further.

[Translation done.]

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Technique

[Description of the Prior Art] As a solid-state polyelectrolyte layer, there is an ion conductivity material represented by the complex of the ion exchange membrane and the polyethylene oxide (PEO is called below) which are represented by the layer (tradename NafionR) of a perfluoro carbon system with a sulfonic group, and an alkali-metal salt, it inquires widely, and the part is put in practical use. Since these layers are solid-states, they do not have a liquid leak, and it is easy to process them, and they have the advantage of being compact. It excels in a thermal property, since that ion exchange membrane, such as a perfluoro sulfonic acid and a perfluoro carboxylic acid, is chemical and the compact cell united with the positive electrode or the negative electrode can be constituted, it is used for a brine electrolysis, and the application to a fuel cell, a water electrolysis, etc. is also considered further. As for the complex of PEO and alkali-metal salts (LiCF₃SO₃, LiClO₄, LiAS F6, etc.), the application to the big rechargeable battery and big primary cell of power density or an energy density, an electrochromic element, or a sensor is expected.

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Effect

[Effect of the Invention] The proton conductive thin film electrolyte of this invention can improve ionic conductivity in a solid thin film electrolyte on the real target which fixed the electrolytic solution during hole.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] By the system using a solid-state polyelectrolyte layer, there is a problem fall for the ohmic loss according [electrical energy luminous efficacy] to membranous electric resistance. Although the solid-state polyelectrolyte layer using an ion conductor like the complex of PEO and an alkali-metal salt has the advantage that it is a solid-state, as compared with aqueous-solution systems, such as a diffusion, alkali, and a salt, in ordinary temperature, a specific conductivity is low 2-3 figures, and intended use is limited from a constraint of a membranous ohmic loss. For example, the effective resistance of an electrolyte layer [as / whose specific conductivities in ordinary temperature are 10^{-6}S and cm^{-1} in a 50-micrometer thickness] is set to 5000ohmcm^{-1} . Although thin film-ization is one solution in order to lower electric resistance, there is mainly a limitation from a constraint of a dynamic intensity. [0004] such a situation — taking an example — this invention persons — the hole of a solid-state macromolecule porous material thin film — although it examines solving the above-mentioned trouble by filling up with and fixing an electrolytic solution in inside, and constituting an electrolyte thin film and a success is stored, in order to aim at utilization of an electrolyte thin film, and an applied expansion, to raise ion conductivity more is desired (Refer to JP,1-158051,A and JP,2-291607,A)

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MEANS

[Means for Solving the Problem] this invention offers the proton conductivity thin film electrolyte which is a solid thin film electrolyte substantially, and is characterized by making the solid electrolyte of proton conductivity which was filled up with the electrolytic solution of proton conductivity and was fixed during hole of a macromolecule fine porosity layer contain or hold on a macromolecule fine porosity layer, in order to attain the above-mentioned technical problem.

[0006] Although high ionic conductivity is obtained since an electrolytic solution is used in spite of being able to deal with substantially the electrolyte thin film which these people are indicating previously like the above as a solid-state, ten to 3 S/about cm is still a limit. On the other hand, H₃PO₄·12H₂O, ZrO(H₂SO₄)₂ and 7H₂O, H₃UO₂PO₄·3H₂O, etc. are known as a proton system ion-conductive-ceramics electrolyte, and the ion conductivity exceeding ten to 3 S/cm is also reported by these. However, these do not remain as they are and cannot necessarily be used as a fuel cell etc. as an electrolyte.

[0007] however, this invention — **** of the above — the usable electrolyte thin film of high ionic conductivity was able to be obtained to the fuel cell etc. by holding on a macromolecule fine porosity layer, and being filled up with the electrolyte of proton conductivity and fixing during hole, the proton system ion conductive electrolyte which has a high ion conductive ceramics. It was also enabled to obtain the high ionic conductivity which exceeds 10–3 S/cm as a solid-state substantially in the thin film electrolyte which can be dealt with by this.

[0008] For 0.1 microns – 50 microns and the rate of a hole, as a macromolecule fine porosity layer, 40 – 90% and breaking strength are [a thickness] 2–200 kg/cm. That whose diameter of a mean breakthrough is 0.001 microns – 0.7 microns is used preferably above. A suitable thickness is 0.1–50 micrometers. Although influenced also by the layer material or the manufacture technique, generally, by less than 0.1 micrometers, it becomes disadvantageous in respect of a practical strength, or handling and workability, and if 50 micrometers is exceeded, effective resistance will become large.

[0009] The suitable rate of a hole is 40 – 90%. At 40% or less, there are too few amounts of a proton conductivity electrolytic solution, and sufficient ion conductivity is hard to be obtained. On the other hand, if 90% is exceeded, it will become difficult to obtain a practical thin film intensity. Breaking strength is 2–200 kg/cm. The above is suitable. Breaking strength makes more difficult than this the parvus, sinking [film production and sinking in of the electrolytic solution] in, or manipulation processing that can be set as a product erector.

[0010] 0.001 micrometers – 0.7 micrometers are suitable for the diameter of a mean breakthrough. It becomes difficult for the parvus and an ion conductive ceramics to become small, and it to fix and carry out transudation prevention of the electrolytic solution, if the diameter of a mean breakthrough is too large on the other hand. As a material of a macromolecule fine porosity layer, polyethylene, polypropylene, a polycarbonate, a polyimide, polyester, tetrafluoro polyethylene, etc. can be used. Although a polyolefine, a polytetrafluoroethylene, and a polyvinylidene fluoride can be used from the field of chemical and an electrochemical stability as a material of a thin film, it is not limited to these. It especially faces using a polyolefine and weight average molecular weight is 5x10⁵. The above polyolefine is suitable.

[0011] As a proton conductivity solid electrolyte supported to a thin film, H₃PO₄·12H₂O, ZrO(H₂SO₄)₂ and 7H₂O, H₃UO₂PO₄·3H₂O, etc. can be used. Moreover, it is not limited to these. for example, about H₃PO₄·12H₂O, and ZrO(H₂SO₄)₂ and 7H₂O·S. There is a report of K Mohapatra, G.D. Boyd, F.G. Storz, S. Wagner and F. Wudl, J. Electrochem. Soc. 126 (1979) 805, etc. Ion ***** of 0.1 [S/cm] is reported by the room temperature. About H₃UO₂PO₄

and 3H₂O, it is A.T.Howe, S.M.Sheffield, P.E.Childs and M.G.Shilton, *Thin Solid Films* 67 (1980) 365. There is an example of a research and there is a report of the ionic conductivity of 5×10^{-3} [S/cm] at a room temperature.

[0012] Although also making a thin film support directly is considered, generally, minerals support is made to support a proton conductivity solid electrolyte, and it holds this to a thin film. What is known as catalyst supports, such as an alumina and a silica, as support can be used. Generally as particle size of support, an about 100–800nm ultrafine particle is good. The above-mentioned thin film is made to specifically fix first the alumina of an ultrafine particle (particle-size:10–80nm), or the support of a silica. As the fixed technique, temperature is raised and pressed, after sprinkling an ultrafine particle uniformly to ** thin film and removing excessive grain by the blower etc. Although temperature differs by the quality of the material and thickness of a thin film, generally about **15 degrees C near a glass transition temperature is desirable.

[0013] ** Infiltrate the precursor of ultrafine particle support, such as a silica and an alumina, into a thin film, and form a silica, an alumina, etc. by the reaction. What is necessary is just to have exposed so that it may be held at a thin film, and it may be under hole in short and an electrolytic solution can be contacted although **** can be carried out. As for the amount of a proton conductivity solid electrolyte, it is desirable to make [many / as possible] it. Proton conductivity electrolytes are the bearers with main ionic conductivity, and it is for raising ionic conductivity by making [many] the amount.

[0014] Fill up the hole of a thin film, and as an electrolytic solution to fix, although the thing others of an indication can be widely used for the aforementioned point ** which these people have already indicated For example, a benzonitrile, benzyl cyanide, a 1-phenyl-1-cyclopropane carbonitrile, DL-2 phenyl butyronitrile, 4-phenyl butyronitrile, 2, and 2-diphenyl propionitrile, Although the solution of the electrolyte which comes to add a proton donor to alkali-metal salts, such as at least one sort and lithium perchlorate of a polyethylene-glycol wood ether and a polypropylene-glycol wood ether, and a sodium perchlorate, and this is usable, it is not limited to this.

[0015] Although an electrolytic solution is proton conductivity in itself, it is during hole of the thin film holding a high proton conductivity solid electrolyte, and has the effect which lowers the interface impedance between high proton conductivity solid electrolytes, and the operation which gives gas-seal nature. The internal organization of the thin film electrolyte of this invention is typically shown in drawing 1 . The support particle 2 is filled up with and held between the macromolecule network structures 1 of a fine porosity thin film, and the proton conductivity solid electrolyte is supported by the front face of this support particle 2. And the electrolytic solution 3 of proton conductivity is filled with the clearance where it remains under hole, and it is placed between the interface of a proton conductivity solid electrolyte.

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EXAMPLE

[Example]

After sprinkling the alumina ultrafine particle of 500nm of mean particle diameters on the 25 micron thick polyethylene fine porosity layer (41% of the rates of a hole, 0.25 micrometers of the diameters of a mean breakthrough, and breaking strength 250kg/cm²) which carried out the example 1 biaxial stretching, and was obtained, it pressurized with the hotpress at 120 degrees C for 60 minutes. Then, since the aqueous solution of 5%-H₃ PO₄12.29(WO₃) H₂ O was infiltrated, it was made to dry at 100 degrees C.

[0017] The solution which mixed the phosphoric-acid aqueous solution and the polyethylene-glycol wood ether by 1:8:1 85% to 2-phenyl butyronitrile was sunk into the obtained support thin film as an electrolytic solution. Consequently, the thin film support electrolyte with which ionic conductivity exceeded ten to 3 S/cm by 3x10 to 3 S/cm was obtained (45 micrometers of thickness).

[0018] In the thin film electrolyte produced without sinking in of an alumina ultrafine particle and H₃ PO₄12.29(WO₃) H₂ O like the above, ionic conductivity was 4.5x10 to 4 S/cm.

[0019] They are after insersion and pressurization and the molybdophosphoric acid H₃ about a silica particle (diameter of 5.5 micrometer) to a polyethylene fine porosity layer like example 2 example 1. Propylene carbonate infiltrated the solution with which [PMo₁₂O₄₀] and nH₂ O consist 40wt%, and a phosphoric acid consists of 10wt% 50%, and produced the electrolyte thin film.

[0020] The ionic conductivity of this electrolyte thin film was 1.01x10 to 3 S/cm. It was the same as that of the above because of the comparison, and when the thin film electrolyte which does not sink in a silica particle and a molybdophosphoric acid was produced, ionic conductivity was 2.47x10 to 4 S/cm.

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DESCRIPTION OF DRAWINGS.

[Brief Description of the Drawings]

[Drawing 1] It is a ** type view inside a thin film electrolyte.

[Description of Notations]

1 — Macromolecule

2 — Support

3 — Electrolytic solution

[Translation done.]

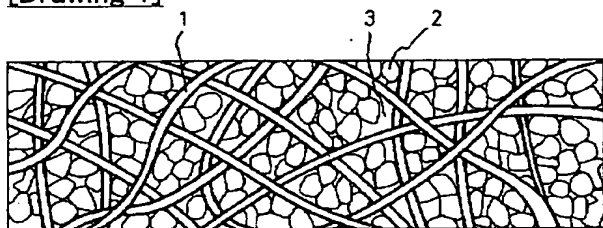
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DRAWINGS

[Drawing 1]



- 1 ... 高分子網状組織
2 ... プロトン導伝性高分子電解質担体
3 ... 電解質溶液

[Translation done.]

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C 0 8 L 101/00				
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(54) 【発明の名称】 プロトン伝導性薄膜電解質

(57) 【要約】

【目的】 薄膜電解質のイオン伝導率を向上させる。

【構成】 高分子微多孔膜にプロトン伝導性固体電解質

[H_3PO_4 (WO_3) $_{12} \cdot 2.9\text{H}_2\text{O}$, $\text{ZrO}(\text{H}_2\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$, $\text{H}_3\text{OUO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$ など] を含有又は保持させ (通常、アルミナ等の担体を用いる)、空孔中にプロトン伝導性電解質溶液を充填、固定する。 10^{-3} S/cm 以上のイオン伝導率が可能である。

【特許請求の範囲】

【請求項 1】 高分子微多孔膜の空孔中にプロトン伝導性の電解質溶液を充填、固定化した実質的に固体の薄膜電解質であり、かつ高分子微多孔膜にプロトン伝導性の固体電解質を保持させたことを特徴とするプロトン伝導性薄膜電解質。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明はプロトン伝導性薄膜電解質に係る。より詳しく述べると、高分子微多孔膜にプロトン導伝性固体電解質を担持し、さらにその空孔中に電解質溶液を含浸してなる薄膜電解質に関し、常温型燃料電池、水電解等の電解質への応用が期待される。

【0002】

【従来の技術】 固体高分子電解質膜としてはスルホン酸基をもつパーフルオロカーボン系の膜（商品名 *Nafion[®]*）に代表されるイオン交換膜やポリエチレンオキサイド（以下 *PEO* と称する）とアルカリ金属塩との複合体に代表されるイオン導電性材料などがあり、広く研究され、一部実用化されている。これらの膜は固体であるために液洩れがなく、加工し易く、コンパクトであるという利点をもっている。パーフルオロスルホン酸やパーフルオロカルボン酸などのイオン交換膜は化学的、熱的性質にすぐれ、正極や負極と一体化したコンパクトなセルを構成できるので食塩電解に利用され、さらに燃料電池や水電解等への応用も検討されている。*PEO* とアルカリ金属塩（ LiCF_3SO_3 、 LiClO_4 、 LiAsF_6 など）との複合体は出力密度やエネルギー密度の大きな二次電池や一次電池、エレクトロクロミック素子やセンサーへの応用が期待されている。

【0003】

【発明が解決しようとする課題】 固体高分子電解質膜を用いる系では電気エネルギー効率が膜の電気抵抗によるオーム損のために低下するという問題がある。*PEO* とアルカリ金属塩との複合体のようなイオン伝導体を用いた固体高分子電解質膜は固体であるという利点があるが、拡散、アルカリ、塩などの水溶液系に比して常温では比伝導率が 2～3 桁低く、膜のオーム損の制約から用途が限定される。例えば、 $50\mu\text{m}$ の膜厚で常温における比伝導率が $10^{-6}\text{ S}\cdot\text{cm}^{-1}$ であるような電解質膜の実効抵抗は 5000 ohmcm^{-1} となる。電気抵抗を下げるためには薄膜化が一つの解決策であるが、主として力学的強度の制約から限界がある。

【0004】 このような事情に鑑みて、本発明者らは、固体高分子多孔質薄膜の孔中に電解質溶液を充填し固定化して電解質薄膜を構成することによって上記問題点を解決することを検討し、成功をおさめているが、電解質薄膜の実用化、応用の拡大を図るためにはイオン導電率をより高めることが望まれる。（特開平 1-158051 号、特開平 2-291607 号公報参照）

【0005】

【課題を解決するための手段】 本発明は、上記課題を達成するために、高分子微多孔膜の空孔中にプロトン伝導性の電解質溶液を充填、固定化した実質的に固体の薄膜電解質であり、かつ高分子微多孔膜にプロトン伝導性の固体電解質を含有又は保持させたことを特徴とするプロトン伝導性薄膜電解質を提供する。

【0006】 前記の如く、本出願人が先に開示している電解質薄膜は実質的に固体として取扱うことができるにもかかわらず、電解質溶液を利用するので高いイオン伝導率が得られるが、それでも 10^{-3} S/cm 程度が限度である。一方、プロトン系イオン伝導性電解質として H_3PO_4 (WO_3) $_{12}\cdot 2.9\text{H}_2\text{O}$ 、 $\text{ZrO}(\text{H}_2\text{SO}_4)_2\cdot 7\text{H}_2\text{O}$ 、 $\text{H}_3\text{O}^+\text{UO}_2\text{PO}_4\cdot 3\text{H}_2\text{O}$ などが知られており、これらでは 10^{-3} S/cm を越えるイオン導電性も報告されている。しかしながら、これらはそのまま電解質として燃料電池などとして使用できるわけではない。

【0007】 しかし、本発明により、上記の如き高いイオン伝導性を有するプロトン系イオン導伝性電解質を、高分子微多孔膜に保持し、かつ空孔中にプロトン導伝性の電解質を充填、固定化することにより、燃料電池などに使用可能な高イオン伝導率の電解質薄膜を得ることができた。これにより、実質的に固体として取り扱うことができる薄膜電解質において、 10^{-3} S/cm^{-1} を越える高いイオン伝導率を得ることも可能になった。

【0008】 高分子微多孔膜としては、膜厚が 0.1 ミクロン～50 ミクロン、空孔率が 40～90%、破断強度が 200 kg/cm^2 以上、平均貫通孔径が 0.001 ミクロン～0.7 ミクロンのものが好ましく使用される。好適な膜厚は 0.1～50 μm である。膜材料や製造方法によっても左右されるが、一般に 0.1 μm 未満では実用強度や取扱い、作業性の面で不利となり、50 μm を越えると実効抵抗が大きくなる。

【0009】 好適な空孔率は 40～90% である。40% 以下ではプロトン導伝性電解質溶液の量が少なすぎて、十分なイオン導電率が得られにくい。一方、90% を越えると実用的な薄膜強度を得ることが困難となる。破断強度は 200 kg/cm^2 以上が好適である。破断強度がこれより小さいと、製膜、電解液の含浸、あるいは製品組立工程における加工処理を難しくする。

【0010】 平均貫通孔径は 0.001 μm ～0.7 μm が好適である。平均貫通孔径が小さいとイオン伝導性が小さくなり、一方、大きすぎると電解質溶液を固定化し、漏出防止することが困難になる。高分子微多孔膜の材料として、例えば、ポリエチレン、ポリプロピレン、ポリカーボネート、ポリイミド、ポリエステル、テトラフルオロポリエチレン等を用いることができる。薄膜の材料としては、化学的、電気化学的安定性の面から例えばポリオレフィン、ポリテトラフルオロエチレン、ポリ

フッ化ビニリデンを用いることができるがこれらに限定されない。ポリオレフィンを用いるに際しては、特に重量平均分子量が 5×10^5 以上のポリオレフィンが好適である。

【0011】薄膜に担持するプロトン伝導性固体電解質としては、 $H_3PO_4 \cdot (WO_3)_{12} \cdot 29H_2O$ 、 $ZrO \cdot (H_2SO_4)_2 \cdot 7H_2O$ 、 $H_3O \cdot UO_2 \cdot PO_4 \cdot 3H_2O$ 等が使用できる。またこれらに限定されない。例えば $H_3PO_4 \cdot (WO_3)_{12} \cdot 29H_2O$ 及び $ZrO \cdot (H_2SO_4)_2 \cdot 7H_2O$ については、S.K.Mohapatra, G.D.Boyd, F.G.Storz, S.Wagner and F.Wudl, J.Electrochem.Soc.126 (1979) 805等の報告があり、室温で $0.1 [S/cm]$ のイオン伝導率が報告されている。 $H_3O \cdot UO_2 \cdot PO_4 \cdot 3H_2O$ については、A.T.Howe, S.M.Sheffield, P.E.Childs and M.G.Shilton, Thin Solid Films 67(1980) 365 の研究例があり、室温で $5 \times 10^{-3} [S/cm]$ のイオン伝導率との報告がある。

【0012】プロトン伝導性固体電解質は直接に薄膜に担持させることも考えられるが、一般的には、無機質担体に担持させ、これを薄膜に保持する。担体としてはアルミナ、シリカ等の触媒担体として知られているものを用いることができる。担体の粒径としては一般に $100 \sim 800nm$ 程度の超微粒子がよい。具体的には、超微粒子（粒径： $10 \sim 80nm$ ）のアルミナまたはシリカの担体をまず上記薄膜に固定化させる。固定化方法としては、

① 薄膜に超微粒子を均一に散布したのち、ブロー等で余分な粒子を除去した後、温度を上げてプレスする。温度は薄膜の材質や厚みで異なるが、一般にガラス転移温度付近 $\pm 15^\circ C$ 程度が好ましい。

【0013】② 薄膜にシリカ、アルミナ等超微粒子担体の前駆体を含浸させ、反応によりシリカ、アルミナ等を形成する。などが実施可能であるが、要は、薄膜に保持され、かつ空孔中で電解質溶液と接触できるように露出していればよい。プロトン伝導性固体電解質の量はできるだけ多くすることが好ましい。プロトン伝導性電解質がイオン伝導率の主な担い手であり、その量を多くすることでイオン伝導率を上げるためである。

【0014】薄膜の空孔に充填し、固定化する電解質溶液としては、本出願人が既に開示している前記先願に開示のものその他を広く使用できるが、例えば、ベンゾニトリル、ベンジルシアナイド、1-フェニル-1-シクロプロパンカルボニトリル、DL-2-フェニルブチロニトリル、4-フェニルブチロニトリル、2,2-ジフェニルプロピオニトリル、ポリエチレングリコールジメチルエーテル、ポリプロピレングリコールジメチルエーテルの少なくとも1種と過塩素酸リチウム、過塩素酸ナトリウムなどのアルカリ金属塩及びこれにプロトン供与体を加えてなる電解質の溶液が使用可能であるがこれに限定されない。

【0015】電解質溶液は、それ自体プロトン伝導性であるが、高プロトン伝導性固体電解質を保持する薄膜の空孔中にあって、高プロトン伝導性固体電解質間の界面インピーダンスを下げる効果と、ガスシール性を付与する作用を有する。図1に、本発明の薄膜電解質の内部組織を模式的に示す。微多孔性薄膜の高分子網状組織1の間に担体微粒子2が充填され保持され、この担体微粒子2の表面にプロトン伝導性固体電解質が担持されている。そして、空孔中の残る間隙をプロトン伝導性の電解質溶液3が充満し、プロトン伝導性固体電解質の界面に介在している。

【0016】

【実施例】

実施例1

二軸延伸して得た25ミクロン厚ポリエチレン微多孔膜（空孔率41%、平均貫通孔径 $0.25 \mu m$ 、破断強度 $250 kg/cm^2$ ）に平均粒径 $500nm$ のアルミナ超微粒子を散布した後、 $120^\circ C$ で60分ホットプレスで加圧した。其の後、5%- $H_3PO_4 \cdot (WO_3)_{12} \cdot 29H_2O$ の水溶液を含浸させてから $100^\circ C$ で乾燥させた。

【0017】得られた担持薄膜に電解質溶液として、2-フェニルブチロニトリルに85%磷酸水溶液とポリエチレングリコールジメチルエーテルを1:8:1で混合した溶液を含浸した。其の結果、イオン伝導率が $3 \times 10^{-3} S/cm$ で $10^{-3} S/cm$ を越えた薄膜担持電解質が得られた（膜厚 $45 \mu m$ ）。

【0018】上記と同様にして、但し、アルミナ超微粒子及び $H_3PO_4 \cdot (WO_3)_{12} \cdot 29H_2O$ の含浸なしで作製した薄膜電解質では、イオン伝導率が $4.5 \times 10^{-4} S/cm$ であった。

【0019】実施例2

実施例1と同様にして、ポリエチレン微多孔膜にシリカ微粒子（ $5.5 \mu m$ 径）を散布、加圧後、モリブドリン酸 $H_3[PMo_{12}O_{40}] \cdot nH_2O$ が40wt%、リン酸が50%、プロピレンカーボネートが10wt%からなる溶液を含浸させて電解質薄膜を作製した。

【0020】この電解質薄膜のイオン伝導率は $1.01 \times 10^{-3} S/cm$ であった。比較のため、上記と同様で、シリカ微粒子及びモリブドリン酸を含浸しない薄膜電解質を作製したところ、イオン伝導率は $2.47 \times 10^{-4} S/cm$ であった。

【0021】

【発明の効果】本発明のプロトン導伝性薄膜電解質は空孔中に電解質溶液を固定化した実質的に固体の薄膜電解質においてイオン伝導率を向上することができる。

【図面の簡単な説明】

【図1】薄膜電解質内部の模式図である。

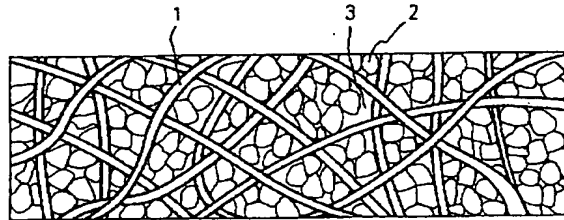
【符号の説明】

1…高分子

2…担体

3…電解質溶液

【図 1】



- 1…高分子網状組織
- 2…プロトン導伝性固体電解質担体
- 3…電解質溶液

フロントページの続き

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